

EPA Comments on Round 2A Field Sampling Plan Surface Water Sampling

General Comments:

The proposed approach calls for the collection of surface water samples using high volume/low detection limit methods at 4 locations for the purpose of evaluating the contribution of bioaccumulative chemicals from known sources within Portland Harbor. This data will be collected during the late summer to maximize the potential for detecting bioaccumulative chemicals that may be discharging to the Willamette River via groundwater transport. However, other contaminant migration pathways at these locations include overland transport of contamination and/or stormwater discharge. Contaminants associated with these pathways would be best captured through a first flush sampling event. Unpublished data generated by Dr. Kim Anderson at Oregon State University suggests that these first flush storm events are a significant source of bioaccumulative chemicals to the Willamette River. As a result, EPA is now requiring the use of low detection limit/high volume sampling techniques during the first two sampling events, late summer and fall. The results of these sampling rounds represent a conservative approach to characterizing potential discharges to surface water. The results of these sampling rounds should be submitted in a timely manner following each sampling event to determine whether additional sampling efforts using low detection limits are necessary.

The sampling approach does not include the collection of VOC data nor the collection of PCB congener data. At this time it is unclear whether this data is necessary to support the RI/FS. However, upon review of groundwater pathway data and PCB aroclor data, EPA may determine that future sampling efforts include these compounds.

The current low detection limit protocol calls for the combining the particulates (captured on the glass fiber filter) with the dissolved portion (captured on the XAD Resin). It states that "at the analytical laboratory the columns and filters will be extracted individually and the extracts will be then pooled into a single composite for the determination of total analyte concentration in surface water." This may result in the loss of a significant amount of information. Performing a separate analysis of each extract will provide information regarding contaminant fate and transport processes at the site by differentiating between dissolved and particulate fractions. In addition, the food web models currently under consideration require the use of "freely dissolved" contaminant concentrations. As a result, both total and dissolved contaminant data should be obtained with the low detection sampling method.

ACGs:

Tribal Comment:

Table 2-3. Method Reporting Limits and Analytical Concentration Goals for Surface Water. We recognize that the LWG accepted EPA's direction of including low detection limit methods and

why are we calling them ACGs?

ACGs. The ACGs that have been included in the FSP for surface water are default values that are not based on site-specific values that have been discussed between LWG, EPA and agency partners. In particular, the human health screening values, upon which many of the low detection ACGs were based, were calculated using inappropriate, generic fish consumption values. The human health screening values need to be recalculated with the tribal fish consumption value of 175 g/day and the ACGs in Table 2-3 updated. Although MRLs may be higher than the ACGs, it is important to follow EPA guidance that indicates that site-specific values be used to develop ACGs when possible.

Dana's Comment:

Gina and I both checked several of the ACGs in the table, especially those for human health. For human health, the screening value for fish consumption is based upon EPA's WQC with an assumed ingestion rate of 17.5 g/day. Given that our highest ingestion rate for the risk assessment is 142.4 g/day, I still recommend that another column be added that uses the default WQC value of 142.4 g/day to develop an ACG for fish consumption. Also (1) the ACGs for the dioxin/furan congeners other than 2,3,7,8-TCDD should be based upon their TEFs; (2) The ACGs for the 2,4' DDD/DDT/DDEs should be the same as their corresponding 4,4' species (3) The ACGs for the chlorinated herbicides are much too high. They are all based upon drinking the water, not on impacts to aquatic life or on the potential for bioaccumulation. There are non-priority AWQC values for some of these for both human health and eco (e.g., in EPA's National Recommended Water Quality Criteria: 2002 (EPA-822-R-02-047) and the gold book. There may be some in ORNL also). These should be added as ACGs and we should ask that the lowest achievable detection limits be used. Several of these chemicals were detected at low levels by USGS in the Willamette River - the LWG's detection limits should be as low as or lower than the detection limits used by USGS. (4) The ACGs for all of the species in technical grade chlordane that do not have WQC for human health (e.g., nonachlors, oxychlordanes) should be identical to the ACG for Heptachlor.

what?

what is this?

Gina and I did not do a thorough review of the ACGs for the ecological screening. We did not review the ORNL values at all. I reviewed most of the values based upon the AWQC for chronic effects - the following reference is given for these values: EPA's National Recommended Water Quality Criteria: 2002 (EPA-822-R-02-047). The values for many of the chemicals listed are not in this reference and it is not clear what their source is. According to Burt Shephard, they may be from some one of the older Gold Books (e.g., lowest observed adverse effect concentrations for phthalates that were not necessarily derived in the same fashion as the AWQC) or from the following reference for PAHs.

Gina's Comment (QAPP):

Table A6- 4 ACGs for surface water analyses

The ACGs listed for surface water in this Table were verified with the EPA Reg 9 PRGs, EPA WQ criteria, Table 2-3 of the FSP and Table 1- Appendix A of the FSP. The following discrepancies were observed.

(Note: When an ORNL value is provided for the metals and it is lower than the WQC value, the ORNL value is not selected.)

arsenic - 0.000018 mg/L from ORNL; ACG listed in Table A6-4 = 0.000045 mg/L
copper - 0.00023 mg/L from ORNL; ACG listed in Table A6-4 = 0.00274 mg/L
nickel - <0.005 mg/L from ORNL; ACG listed in Table A6-4 = 0.016 mg/L
zinc - 0.030 mg/L from ORNL; ACG listed in Table A6-4 = 0.0365 mg/L

Please reconcile the specified ACGs in the QAPP with ACGs listed in the FSP.

QAPP Comment:

The LWG accepted EPA's direction to include low detection limit methods and alternative concentration goals (ACGs) for surface water. The ACGs that have been included in the QAPP are default values that are not based on site-specific parameters that have been discussed between LWG, EPA and agency partners. In particular, the human health screening values, upon which many of the low detection ACGs were based, were calculated using generic fish consumption values. The QAPP should note that higher fish consumption rates have been agreed to in the programmatic work plan and that site specific data generated and food web modeling may require adjustment of ACGs in subsequent surface water sampling efforts.

Proposed Comment:

The alternative concentration goals (ACGs) presented in Table 2-3 are based on chronic ambient water quality criteria (AWQC) or Oak Ridge National Laboratory (ORNL) screening values for ecological receptors and AWQCs based on fish consumption or Region 9 Preliminary Remediation Goals (PRGs) for human health.

In some cases (e.g., arsenic, copper, nickel and zinc), the ORNL number is below the chronic AWQC. In other cases, (e.g., chlorinated herbicides) ecological screening criteria are not available. Laboratory minimum reporting limits (MRLs) for these chemicals should achieve lower the ORNL screening values and other appropriate screening levels (e.g., Gold Book values) to the extent feasible using the methods described in the Round 2 Quality Assurance Project Plan (e.g., EPA Method 6020, ICP/MS and EPA Method 8151).

For bioaccumulative chemicals, the Level 2 ACGs are based on a generic fish consumption rate of 17.5 grams per day. Fish consumption rates specified in human health risk assessment (HHRA) work plan (Appendix C of the Programmatic RI/FS Work Plan) range from 17.5 to 175 g/day. As a result, it not possible to determine whether the Level 2 ACGs will result in concentrations protective of human health. In addition, because the Round 2 QAPP does not

specify laboratory minimum reporting limits and pumping volumes associated with the XAD II high volume/low detection limit sampling technique, it is not possible to determine the feasibility of achieving AWQCs adjusted to reflect site specific fish consumption rates. In addition, EPA has not performed a detailed review of the Round 1 data to identify those contaminants that are present in fish tissue at levels that may pose a risk to human health or the environment.

The Surface Water FSP should note that the ACGs are default values based on a generic fish consumption rate and do not represent the higher fish consumption rates included in the HHRA work plan. In addition, the Surface Water FSP should evaluate the feasibility of achieving AWQCs adjusted to reflect these site specific fish consumption rates using the XAD II resin high volume/low detection limit sampling method.

It should be noted that the results of the Preliminary Risk Evaluation, food web model, Round 2 Site Characterization Summary and other interim RI/FS deliverables will determine whether the surface water detection limits were adequate based on the collection of site specific data. If it is determined that these detection limits are not adequate, further characterization of surface water may be required.

Specific Comments:

Section 1.0 - Introduction; Page 1: There is no technical or programmatic basis for defining surface water as "occurring from 1 meter from above the river bottom to 0.3 meter below the water surface." All references to this definition should be removed from the surface water FSP and associated QAPP. It is more appropriate to state that the proposed sampling methodology is designed to characterize surface water.

Section 2.1, Data Needs; Pages 4 and 5:

The FSP states that surface water data will be used in the ecological risk assessment to evaluate effects associated with direct toxicity. However, the surface water data will also be used to support the food web model and may be used to understand the contribution of surface water to observed fish tissue concentrations and the associated risk to piscivorous wildlife.

The FSP also states that the surface water data will be used to evaluate risk to human health resulting from direct contact with and incidental ingestion of surface water. As described above, the data will also be used to support the food web model. The FSP should describe the use of surface water data to support the food web model, especially as it relates to detection limits. In particular, chemicals detected in surface water must be compared to ambient water quality criteria for the protection of human health for fish consumption since these standards in addition to the EPA Region 9 tap water PRGs. ?

The collection of surface water data to evaluate the contribution from specific sources should also be included as a data need.

what is this saying?

The term "water particulate chemistry" in the FS data needs section should be modified to clarify that it refers to contaminants sorbed to entrained sediment particles.

Section 2.2, Sample Types and Numbers, Pages 5 through 7:

What does this comment mean?
In addition to posing a threat to human health, hydrophobic COIs may also pose a threat to piscivorous wildlife. Although standard MRLs may detect concentrations of COIs that are protective of aquatic life, standard MRLs may not be able to detect COIs protective of piscivorous wildlife.

Near bottom samples should be as close to the bottom as practical to not include sediments, not arbitrarily set at "within 1 meter of the river bottom" particularly if the objective is to support the ecological risk assessment. As stated in EPA's December 19, 2004 letter, samples collected to support the ecological risk assessment and the source evaluation should be collected 1 foot off the bottom of the river, not one meter. This is also consistent with Figure C-2 of the Surface Water FSP. Samples collected to evaluate amphibians in support of the ecological risk assessment should be collected as close to the river bank as practicable and no deeper than 20' below the river surface.

Single-point water-column samples should be integrated for the water column between the ranges of one foot below the surface to 1 foot above the river bottom. These samples are to support the human health risk assessment and swimmers could potentially be at any depth. It is unclear whether samples will be integrated spatially. It is recommended that surface water samples collected to evaluate source contributions and to support the human health and ecological risk assessments be spatially integrated. This will result in the collection of a more representative surface water sample.

The referenced text states "all high volume samples collected with a XAD-2 column will be considered unfiltered." As stated in the general comment above, combining the filter extract with the dissolved form will result in the loss of information necessary to support the contaminant fate and transport evaluation and the food web model.

The frequency of sampling should be discussed more thoroughly in this section. The narrative should reference Table 2-1. Perchlorate should be sampled offshore of the Atofina facility during the summer and fall sampling events.

Section 2.3 Sample Analyses - General Water Quality Measurements: The FSP should state that general water quality measurements will be made in-situ by lowering the appropriate probe into the water (as stated in Appendix E). This statement should also be made in Sections 3.6.1, 3.6.2 and other applicable sections of the FSP.

3.6.2 Summary of High-Volume Surface Water Sampling (with XAD-2 columns) Method; Page 14:

The FSP should note that general water quality measurements will be made at high volume sampling locations in addition to the sampling locations described in Section 3.6.1.

Pumped sample volumes and pumping rates are based on the analytical concentration goals and laboratory MRLs. However, MRLs are not included in this document. Pumping volumes must be adequate to achieve the specified ACGs. In addition, it should be noted that the human health AWQCs for bioaccumulative chemicals are based on a fish consumption rate of 17.5 g/day. Fish consumption rates to be used in the human health risk assessment range from 17.5 to 175 g/day. Pumping rates should be adjusted accordingly.

The last sentence on this page states that, "Pumped sample volumes and pumping rates for each analyte will be predetermined based on the analytical concentration goals and laboratory MRLs." Both the laboratory MRLs and the pumping volumes/rates are missing from this FSP and the QAPP. We should only provide a conditional approval of this FSP and the QAPP for surface water until we see these MRLs and pumping information.

Section 3.7 - Sample Identification Page 15: Sample numbering scheme should be "SW" not "W" to allow for the collection of other water samples (i.e., groundwater and porewater).

Section 4.0 - Reporting: Data reporting must be consistent with approved schedule in programmatic work plan.

Figure 2-1b - Proposed Sample Locations: Sample W-16 should be moved upstream to a point just downstream of the upstream Atofina dock. This will optimize the potential for detections of contaminants associated with the Atofina facility.

Table 2-1, Summary of Round 2A Surface Water Samples and Analyses: This table should note that additional trace samples may be required for bioaccumulative chemicals depending on the results of the two initial low detection limit analyses.

Table 2-2 - Round 2A Surface Water Sampling Summary: The table should make it clear that Sample W-12 will be used to evaluate contaminant discharges from GASCO in addition to being a beach area sample. Similarly, samples W-1 W-6, and W-17 may also be used to evaluate contaminant discharges from Oregon Steel Mills, Kinder Morgan and Willbridge respectively. In addition, further elaboration regarding changes in the location of sample W-18 should be provided in the text of the FSP.

Table 2-3, Method Reporting Limits and Analytical Concentration Goals for Surface Water: Additional information regarding "MRL1" and "MRL2" should be included in the footnote and in the text of the FSP.

Appendix B - Transect Composite Surface Water Sampling Method for Round 2A:

The appendix should provide information to support the number of increments in each transect. As noted in the text, USGS recommends a minimum of four increments. However, the USGS guidance it also states that the number chosen should not be chosen arbitrarily, but should be based on consideration of a number of factors, including the data objectives for the study.

The approach for horizontally integrating sample collection within each equal-discharge increment (EDI) should be described. Based on the description, it is unclear whether vertically integrated samples will be collected at the center point of each EDI or whether samples will be collected on a horizontally integrated basis within each EDI.

EPA Comments on Round 2 QAPP:

Although EPA submitted comments on the Round 2 QAPP earlier, we were unable to provide comments related to the surface water sampling program. As stated in our comments:

“At this time, the EPA and its partners are still reviewing the Round 2 Surface Water FSP. In addition, key elements of the Round 2 QAPP related to surface water have not been provided pending selection of a surface water laboratory. These include laboratory methods, method detection limits (MDLs), method reporting limits (MRLs) and the surface water laboratory Quality Assurance Manual. EPA and its partners will be commenting on a number of elements related to the Round 2 QAPP in its comments on the Round 2 Surface Water FSP. It is EPA’s expectation that our comments on the Round 2 Surface Water FSP will be incorporated into the revised QAPP.”

As a result, we are including a set of general and specific comments related to the Surface Water elements of the Round 2 QAPP. Approval of the Round 2A Surface Water FSP is contingent on approval of the Round 2 QAPP.

General QAPP Comments:

Once the laboratory has been selected for surface water sampling, MDL studies and initial demonstration of capabilities (IDCs) at the water quality criteria levels of the laboratories selected for surface water analyses per instrument must be submitted by LWG to EPA in the revised Round 2 QAPP.

The Round 2 QAPP should discuss the rationale for selecting stations for splits and field replicate surface water samples.

The QAPP does not adequately state the project objectives for surface water and how these objectives will be achieved. The Round 2 QAPP should include sampling rationale (including the rationale for the selection of sampling stations and which stations are sampled using high volume (XAD-2) samplers) described in the Round 2 Surface Water FSP.

Specific QAPP Comments:

Section A6.1.3 - the last 4 paragraphs of this section describing the sampling scheme for surface water are vague and confusing and will need major revision. Also, the rationale for the selection sampling stations, choosing the two methods of surface water sample collection and the sampling scheme are clearly discussed in the FSP. Please incorporate these information in the QAPP.

Example outline of sample collection scheme (Note: This example used the information provided in the Surface Water FSP pages 6-8; Figures 2-31a, 2-1b, 2-1c and Tables 2-1 and 2):

Summer Sampling:

XAD-2 (high volume) samples

3 transects, Willamette Cove and Rhone-Poulenc - will be analyzed for low level (ACG2) dioxins and furans, PCB as Aroclors, SVOCs, PAHs, phenols, phthalates, herbicides and TBTs. High volume samples from stations near Atofina and Portland Shipyard will also be analyzed for PCB as Aroclors, SVOCs, PAHs, phenols, phthalates, herbicides and TBTs

Peristaltic pump samples - regular detection limits (ACG1)

Sampling stations are 13 ERA, 3 HHRA, 3 transects, Rhone-Poulenc , Willamette Cove, Atofina, and Portland Shipyard (23 stations total). Twenty-three unfiltered water samples will be analyzed for total metals, TSS and TOC with standard detection limit (ACG1) levels. Filtered water samples collected from 23 stations will be analyzed for dissolved metals, TDS, DOC and hardness at the standard detection limit (ACG1) levels. Unfiltered samples collected from 13 ERA and 3 HHRA will be analyzed for regular ACG1 PCB as Aroclors, SVOCs, PAHs, phenols, phthalates, herbicides, TBTs. Perchlorate will also be analyzed for the station near Atofina.

Fall Sampling:

XAD-2 (high volume) samples

3 transects for low level (ACG2) dioxins and furans, PCB as Aroclors, SVOCs, PAHs, phenols, phthalates, herbicides, TBTs.

Peristaltic pump samples - regular detection limits (ACG1)

13 ERA, 3 HHRA, the station replacement for W18 (Portland Shipyard) and 3 transects - total 20 unfiltered samples will be analyzed for PCBs as Aroclors, SVOCs, PAHs, phenols, phthalates, herbicides, TBTs, total metals, TSS, and TOC. Filtered samples from 20 stations listed above will be analyzed for dissolved metals, TDS, DOC and hardness. Perchlorate will

also be analyzed for the station sample near Atofina.

Winter sampling:

XAD-2 (high volume) samples

3 transects for low level (ACG2) dioxins and furans, PCB as Aroclors, SVOCs, PAHs, phenols, phthalates, herbicides, TBTs.

Peristaltic pump samples - regular detection limits (ACG1)

13 ERA, 3 HHRA, the station replacement for W18 (Portland Shipyard) and 3 transects - total 20 unfiltered samples will be analyzed for PCBs as Aroclors, SVOCs, PAHs, phenols, phthalates, herbicides, TBTs, total metals, TSS, and TOC. Filtered samples from 20 stations listed above will be analyzed for dissolved metals, TDS, DOC and hardness. Perchlorate will also be analyzed for the station sample near Atofina.

Tables A7-1 and A7-2, Note in this Tables that full target list will be spiked into the LCS, LCSD, MS and MSD QC samples except for the PCB as Aroclor analyses which uses Aroclors 1016 and 1260 as the spike compounds.

Table B2-1 The recommended preservation for water samples for mercury analyses using the Method 1631E is the addition of 5 ml/L of pretested 12N HCL or 5 ml/L of BrCl solution to the sample bottle. The holding time using this method and preservation technique is 90 days.

Table B2-2 (1) The QC for TOC analysis is triplicate analysis of one sample per 20; (2) include mercury in this table- check Method 1631E for preservation and the holding time is 90 days (3) the holding time for Chromium VI is 24 hours, discuss how will LWG ensure that the water samples for Cr VI will not exceed holding times (4) the CWA, SDWA and RCRA holding time for 2,3,7,8-TCDD in water (40 CFR 136) is 7 days from sample collection date and additional 40 days after extraction. Please make the necessary corrections to this Table and footnotes.

Table B4-3 This table must be consistent with Table 2-1 of FSP. In addition, filtered samples will need separate QC samples from unfiltered samples. Please specify in this Table the analyses that will use filtered and unfiltered samples and the corresponding numbers of split and replicate samples.